SCIENCE FOR CERAMICS PRODUCTION

FEATURES OF HIGH-DENSITY INDUSTRIAL CERAMICS TECHNOLOGY. SELECTION OF MODIFYING ADDITIVES

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The effect of modifying additives on sintering, microstructure control, and the properties of ceramics was demonstrated. The types of additives with a different type of reaction with the crystal lattice of the basic oxide in sintering were examined. Oxides that form solid solutions are the most effective additives that significantly affect sintering and microstructure formation processes.

The attempt to determine the possibilities of controlling the microstructure of ceramics has led investigators to use a large number of modifiers and to study the effect of their concentration and the character of the interaction on sintering and the properties of products. These studies allowed accumulating a large amount of experimental data and creating a number of ceramic materials which are still used in industry. However, no system has yet been developed for selecting additives to attain these goals, although the acquired experience allowed moving significantly forward in understanding strengthening and densification and establishing measures which to some degree make it possible to affect them. The published data is frequently somewhat contradictory, which is due to flawed methods of incorporating the additives that do not ensure their uniform distribution in most cases. For this reason, when the same substances are used in the same quantities but with different methods, their effects can differ significantly.

As a function of the character of the reaction with the crystal lattice of the basic oxide at the sintering temperatures, additives can conveniently be divided into four groups: 1) totally soluble; 2) insoluble but forming a liquid phase due to melting or reaction with formation of an eutectic melt; 3) insoluble and not reacting (inert additives); 4) forming crystals of a new chemical compound [1].

Additives in the first group, widely used to increase the solid-phase sintering rate, chiefly act by changing the con-centrations of vacancies in the cationic or anionic sublattices of the crystal. Additives in the second group accelerate the processes as a result of intensifying mass transfer in the presence of a liquid phase. The additives incorporated in the region of eutectic compositions are very interesting, since finely crystalline materials consisting of two or more phases and having specific properties can be obtained in this case. The additives in the fourth group can accelerate or slow sintering as a function of the nature of the new compound formed.

Use of modifying additives from the first group is most interesting for industrial ceramics technology as this allows controlling the densification rate, especially its final stage when the microstructure of the material is formed. It is believed that not all additives capable of forming defects can intensify sintering. In heteroionic materials such as oxides, the rate of this process is controlled by diffusion of either the oxygen cation or the anion. For this reason, the additive should increase the concentration of the concrete defect, but it is somewhat difficult to determine the type. In polycrystalline materials, the rate of solid-phase processes is controlled by diffusion of cations in most cases. A similar mechanism has been established for aluminum, magnesium, zinc, and other oxides. Oxygen can easily diffuse over the boundaries of the crystals. It can sometimes be intensified by the appearance of nonstoichiometric vacancies in the anionic sublattice in sintering in a vacuum or oxygen [2].

In incorporation of soluble additives, solid substitution or interstitial solutions can be formed with the basic oxide. In the first case, the lattice parameters of the basic and added oxides with a difference in the cation radii no greater than

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TABLE 1

Composition* of the ceramic	Lattice parameter, nm		Change in parameter, %		Stresses arising in lattice, MPa
	yttrium oxide	solid solution	linear	volume	
$0.9Y_2O_3 - 0.1ZrO_2$	1.0603	1.0586	− 0.160	− 0.48	+ 320
$0.9Y_2O_3 - 0.1HfO_2$	1.0603	1.0582	− 0.198	− 0.59	+ 400
$0.947Y_2O_3 - 0.053Eu_2O_3$	1.0596	1.0630	+ 0.320	+ 0.96	− 640
$0.7Y_2O_3 - 0.3Gd_2O_3$	1.0605	1.0668	+ 0.594	+ 1.78	− 1200

* Molar content.

15% should be close [3]. The second case is possible when the size of the additive cation is much smaller than the cation of the basic oxide; such systems are rarely encountered. When the charges of the additive and basic oxide cations are the same, isovalent substitution (introduction) is involved, and defects do not arise. If the charges are different, heterovalent substitution is observed. There is usually a restricted solubility region, and formation of solid solutions is accompanied by the appearance of vacancies or ions in interstices [4].

Sintering of oxides with additives forming solid solutions differ slightly from sintering of pure oxides in which crystal growth begins long before the pores are totally eliminated and they "collapse" inside. It is usually believed that nonporous materials can only be obtained when crystal growth can be restricted; in this case, pores can go out to the boundary by diffusion [5].

Different models have been proposed for explaining the role of additives in sintering. The "second phase" model hypothesizes that the layers of the second phase formed in the reaction that are separated along the crystal boundaries prevent crystal growth in the final stage [6]. The "aggregation of dissolved elements" model hypothesizes that the additive is concentrated on the boundaries of the crystals and prevents them from growing [7]. The "solid solution" model hypothesizes that the sintering rate increases significantly in comparison to the crystal growth rate due to the sharp increase in the diffusion coefficient when the additive dissolves [8].

In our opinion, the "solid solution" model is the most reliable, since the sharp increase in the rate of pore elimination in the intermediate stage of sintering, when the diffusively-viscously deformed particles are aligned with each other, and not restriction of crystal growth as such, plays the deciding role in obtaining a nonporous ceramic. There is usually almost no crystal growth. The additives dissolved in the crystal lattice ensure high diffusive mobility of the particles by increasing the concentration of vacancies by several orders of magnitude in comparison to the thermally equilibrium concentration. The highest density, as well as high transparency of the materials with preservation of monophasicity, are only ensured in this case. In addition, they allow varying the microstructure and strength characteristics of the ceramic within wide limits.

A transparent (i.e., highly dense) ceramic can be made from several oxides by incorporating cations of different valence. For example, such a ceramic is made from yttrium oxide using 0.1 – 0.8% (mass content) BeO, 2 – 5% (mass content) Eu_2O_3, 20 – 25% (molar content) Gd_2O_3, and 2 – 15% (molar content) HfO_2 as additives. They all form solid solutions with yttrium oxide (see Table 1). If we hypothesize that cationic vacancies should arise, the types of solid solutions should differ significantly in the systems indicated above. The beryllium cation has a small ion radius so that when it is incorporated in yttrium oxide, a solid interstitial solution can be formed with the appearance of vacancies with respect to the yttrium.

For an yttrium oxide ceramic with hafnium (zirconium, thorium) oxide additives, it was experimentally shown that after firing in air medium, a solid substitution solution with interstitial oxygen is formed. There are no cation vacancies, and this could explain the low degree of sintering of the samples at temperatures up to 1750°C. At the same time, they acquire almost the theoretical density and become transparent in a vacuum. In these conditions, the stoichiometry with respect to oxygen is perturbed in the yttrium oxide, and the concentration of oxygen vacancies increase, and conditions are created for passage of interstitial oxygen into them as a result. Negatively charged cationic vacancies should be formed to compensate for the positive charge. The appearance of a certain concentration of cationic vacancies is probably sufficient to ensure obtaining a nonporous transparent ceramic.

When europium oxide is incorporated in yttrium oxide, a solid substitution solution is basically formed, but on sintering in a vacuum, slight reduction of trivalent europium to divalent europium is observed, and this can cause the appearance of a solid interstitial solution with the appearance of cationic vacancies. This possibility is confirmed experimentally by comparing the pycnometric and x-ray densities.

In incorporation of gadolinium oxide, the transparency, i.e., the effect of total elimination of pores, appears with important amounts of the additive. A solid isovalent substitution solution is formed with an increase in the lattice parameter by approximately 0.6%. The stresses in deformation of the lattice probably cause the appearance of vacancies of both signs, which significantly accelerates sintering.

An additive incorporated in yttrium oxide for obtaining it in transparent form should thus form a solid solution of a determined type. Its lattice parameter sometimes varies by more than 1% (see Table 1).

The crystal lattice of the oxide is in a strongly stressed state when the additive dissolves, and these stresses are unevenly distributed locally, since the greatest movements of the lattice elements involve the site of the substituted ion. The presence of tensile stresses ensures high mobility of the atoms, which has a decisive effect on diffusion mass transfer

[9]. An important increase in the concentration of lattice defects is the cause of intensification of diffusion over the surface and bulk of the particles, and this probably facilitates their slipping and subsequent adjustment.

The yttrium oxide ceramic with a density close to the theoretical density and high transparency is obtained when other additives than those in Table 1 are added to the solid solution. The role of the additives with respect to their crystal chemical features, electronegativity value, and character of the reaction with the basic matrix is seen in this example. Heterovalent additives are effective in small quantities — from 0.1 to 5.0% (molar content). This is due to the formation of defects in the crystal lattice, which significantly accelerates all diffusion processes. The ceramic obtained is usually characterized by a finely crystalline structure. The effective effect of isovalent substitution additives is manifested in important amounts — up to $20 - 30\%$ (molar content), probably when sufficient stresses arise to increase the mobility of the atoms. In these cases, the microstructure is relatively coarsely crystalline.

The features of the effect of the additives that form the solid solutions established in sintering of Y_2O_3 and allow obtaining materials with the theoretical density are completely confirmed in studying sintering of Se_2O_3 with ZrO_2, HfO_2 additives and combined Y_2O_3 and HfO_2 additives. The amount of additives is approximately the same as in incorporation in yttrium oxide.

N. M. Pavlushkin [10] investigated the effect of 53 additives to corundum on its sintering, structure, and transparent properties. It was found that only MgO in the amount of $0.5 - 1.0$ wt.% allows obtaining finely crystalline ($3 - 5$ μm) and high-strength ceramics (the bending strength attains 450 MPa) in brief, high-temperature firing. This was the only ceramic material (microlite) widely used up to now as a construction ceramic (cutting tools, dies, etc.). Subsequent studies concerned selection of the additive and methods of incorporation to create a nonporous structure, including transparent ceramics. Magnesium oxide added in the amount of $0.01 - 0.25\%$ (mass content) was the basic additive used in all cases. The materials Lucalox (USA) and Polikor (USSR) of similar composition and technology were developed. However, in successive studies, preference was given to double additives, one of which was always MgO.

The mechanism of action of MgO additive, despite the many studies, has still not been completely explained. The fundamental opinion is that the MgO reacts with Al_2O_3 with formation of a noble spinel distributed over the boundaries of the crystals, which prevents them from growing and causes their characteristic isometric shape and relatively small size [11]. However, there is also evidence of the uniform distribution of MgO in the bulk. The types of solid solutions examined in the literature are hypothetical due to the low concentration of MgO. It is almost impossible to accurately determine the changes in the lattice parameters of aluminum oxide. We can hypothesize that the character of the distribution

of MgO in the crystals will be a function of the method of its incorporation and can attain uniformity in the corresponding conditions. There is probably a small region of solubility of MgO in Al_2O_3. If we consider the opinion concerning the determining role of diffusion of oxygen in sintering of corundum, we can hypothesize the formation of a solid substitution solution with the appearance of oxygen vacancies, which will also accelerate the process.

The possibilities of regulating the microstructure of Al_2O_3 by creating solid solutions are extremely limited, since only a small number of oxides form solid solutions with Al_2O_3 in a wide enough range of compositions; we can only name gallium, chromium, and scandium oxides.

Additives whose cations have a higher charge than the magnesium cation are basically used in fabricating nonporous transparent magnesium oxide. The best results are obtained with Y_2O_3 and Se_2O_3 additives. In simultaneous formation of solid iso- and heterovalent substitution solutions, the sintering rate, character of crystallization, and strength properties of periclase ceramic can change significantly. NiO and ZnO combined with Se_2O_3 or Y_2O_3 are similar additives. Based on research experience, we can hypothesize that the molar content of NiO or ZnO additive (isovalent substitution) should be $15 - 25\%$, while the amount of the second additive (heterovalent substitution) should be $0.1 - 0.5\%$. Actually, at a firing temperature of $1500 - 1550°C$ in a vacuum or hydrogen medium, a ceramic with high density and transparency is obtained (porosity of approximately 1%, bending strength of 200 MPa). Firing at 1500°C in oxygen medium results in a transparent material with bending strength of $180 - 200$ MPa. The additives have cations with a larger radius than the magnesium cation, and for this reason, formation of a coarsely crystalline microstructure (crystal size of $30 - 50$ μm) is observed.

Similar principles for increasing the degree of sintering are used in production of ceramics from zirconium oxide. The additives preserve the crystal lattice and high-temperature cubic form, creating anionic vacancies in it, since the stabilizing oxides have a cation with a charge of 2+ or 3+ (for example, MgO, CaO, Y_2O_3, Sc_2O_3, etc.). One important possibility of intensifying the sintering process up to total elimination of porosity is to use combined additives, for example, TiO_2 or CeO_2 combined with Y_2O_3 or La_2O_3. Titanium and cerium oxides form solid solutions with zirconium dioxide in a wide range of compositions and can cause important stresses in the crystal lattice. It is necessary to consider that it is easily reduced in gaseous medium with a low partial oxygen pressure. A nonporous transparent ceramic can be obtained from zirconium dioxide with addition of 20% CeO_2 and 5% Y_2O_3 (molar content) in sintering in oxygen medium at 1700°C.

We note that the proposed principle for increasing the degree of sintering of oxides by incorporation of additives that simultaneously form solid iso- and heterovalent substitution solutions allows establishing new compositions of oxide ce-

ramic materials that can be sintered to a pore-free state. Some general rules in selecting additives that cause sintering to high density and even to total elimination of pores are also observed for oxide compounds. The analysis shows that almost all substances added, for example, to $MgO \cdot Al_2O_3$ or $3Y_2O \cdot 5Al_2O_3$ can form solid solutions in one of the sublattices of the oxide compound.

To obtain a transparent ceramic based on $MgAl_2O_4$ noble spinel, Y_2O_3, Cr_2O_3, CaO, MgO, Sc_2O_3, SrO, and rare-earth element oxides are added. Yttrium oxide has some solubility in MgO, Cr_2O_3 is soluble in MgO, and MgO is soluble in Al_2O_3; Sc_2O_3 dissolves in all oxides making up the compound; SrO should dissolve in MgO; some REE oxides dissolve in MgO (Nd_2O_3, for example). Incorporation conditions where the additives will dissolve in the sublattice of the oxide with which they form a solid solution, i.e., are incorporated in nodes corresponding to the ion radii, can also be created. Substances which dissolve in the sublattice of the magnesium and thus create a high concentration of vacancies in the aluminum sublattice especially favorably affect elimination of porosity; for example, incorporation of scandium oxide in an amount of less than 0.5% (mass content) results in a transparent ceramic.

Additives which can significantly improve sintering of oxides, including up to total elimination of porosity, should thus be added to solid solutions. In formation of heterovalent solid solutions, their molar content is usually 0.1 – 5.0% and 15 – 30% for isovalent solid solutions. In the last case, the oxides of elements in one subgroup or (for those having a cation charge of 3+) REE oxides can be used. For heterovalent solid solutions, the oxides of elements usually in adjacent subgroups or REE oxides can be used. It should be noted that an important effect is observed in all cases when oxides whose cations have large differences in the ion radii are used, as this ensures the appearance of important stresses that facilitate diffusion processes in the lattice of the basic oxide. When combined additives are incorporated, the proposed principles still hold, only they are joined in one matrix which significantly enhances their effect on elimination of porosity in sintering. In most cases, simultaneously iso- and heterovalent substitutions are used, and almost nonporous materials which have sufficiently high (sometimes extremely high) transparency combined with high strength are obtained.

Determination of the type of solid solutions in different oxide systems showed that the effect of the type on sintering is practically small, which to some degree is not in agreement with the published concepts. The type of solid solution formed on addition of an additive from crystal chemical theoretical conditions is probably not important in most cases, while the gas medium in which the articles are fired by implementing the mechanism (chemistry) of occurrence of the concrete reaction is of major importance. Oxide materials with a cubic crystal lattice sinter to the transparent state in a vacuum or in oxygen regardless of whether or not structural defects are formed. In isovalent substitution, stresses that in-

crease the rate of diffusion processes play the basic role in sintering. In formation of a solid solution in anisotropic oxide materials, the size of the crystals deceases; due to the nonuniform change in the lattice parameter, they become isometric.

We note that the powder preparation technology, which in most cases should ensure the uniform distribution of the additives over the bulk of the particles, becomes extremely important. This can only be attained with chemical methods. Based on an analysis of the published data and the experience from our studies, precipitation of poorly soluble compounds by spraying concentrated hot solutions in a precipitator is the most promising method which will ensure obtaining highly disperse unaggregated powders with uniformly distributed components. In all cases of using this method, a significant effect was obtained in increasing the density, transparency, and strength and decreasing the sintering temperature. It is necessary to note that no quantitative mechanisms can be established at present due to the large number of factors that affect the occurrence of a multistage process that ends in sintering.

The basic principles that determine intensification of sintering can be briefly formulated as follows. The incorporated additive should form a solid solution, and cations of the additive and basic oxide should have as great a difference in the ion radii as possible. The molar content of the heterovalent additive in the solid solution is within the limits of 0.1 – 5.0% and the content of the isovalent additive is 15 – 30%. The simultaneous use of iso- and heterovalent substitutions significantly enhances their effect. The amount of additives is usually the same as when they are added separately. It is necessary to exclude formation of new compounds here. These basic assumptions can be used in incorporating additives in oxide compounds; the process methods must ensure formation of solid solutions in the corresponding sublattices.

Using the proposed principles, solid solutions were synthesized in the $Al_2TiO_5 - Sc_2O_3$ system in which it was possible to sharply restrict growth of aluminum titanate crystals (from 60 – 70 to 5 μm) and increase the bending strength to 100 MPa (without the additive, it was 20 MPa due to formation of a microfractured structure) at a mass content of 15 – 20% Sc_2O_3. This example graphically demonstrates the possibilities in controlling the microstructure and properties of ceramic oxide materials on addition of modifying additives.

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